Evidence for Size Effects on Interfacial Widths in Confined Thin Films

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When a film of thickness D of a binary mixture on a substrate segregates into two coexisting phases, an interface between the phases parallel to the substrate may form due to preferential surface attraction of one of them. It is argued then that the correlation length $\xi_\parallel$ for interfacial fluctuations parallel to this interface ($\ln\xi_\parallel \propto D$) leads to a size-dependent interfacial width $w \propto \sqrt{D}$. Nuclear reaction depth profiling experiments on polymer mixtures as well as Ising model simulations both support this prediction. [S0031-9007(96)00723-5]

Thin films on substrates find various technological application in materials science and also pose challenging fundamental problems, since the combination of size and surface effects may lead to properties that differ very much from the bulk [1–6]. For example, consider a binary (*AB*) mixture which may undergo a phase separation into two phases (*A* rich with an *A* volume fraction ϕ_2, and *A* poor, ϕ_1, respectively) below some critical temperature T_{cb} in the bulk [4–6]: In a thin film geometry, the substrate may prefer one of the coexisting phases [5] and can hence stabilize an interface between them, such that the interface (on average) is parallel to the substrate. The interplay between phase separation and wetting [7] in this geometry has recently been studied theoretically [4], experimentally [5], and by simulations [6], and has stimulated considerable discussion [8,9].

It is believed that in the temperature region below T_{cb}, but above the wetting temperature T_w of a semi-infinite system, there should exist a kind of "soft mode phase" [4] that is associated with a freely fluctuating interface, i.e., unbound from the constraining walls of the film. This phase is characterized by an anomalously large correlation length $\xi_\parallel$ for concentration fluctuations in the directions parallel to the substrate [4,6,9],

$$\xi_\parallel = \xi_b \exp(\kappa D/4), \qquad (1)$$

ξ_b being the correlation length at the coexistence curve of a corresponding bulk system, D is the film thickness, and the transverse length scale κ^{-1} in mean field theory [4] is simply $\kappa^{-1} = \xi_b$ but gets enhanced by fluctuations if one goes beyond mean field [6,9,10]. The reason why the lateral correlation length $\xi_\parallel$ increases with increasing film thickness may be viewed, at a qualitative level, as having to do with the energy cost of truncating the local interfacial composition profile between the coexisting phases by one of the film boundaries. This "truncation effect" is weaker in thicker films—where the film boundaries are more distant from the mean position of the phase interface—

resulting in a correspondingly larger lateral correlation length [4].

The anomalous enhancement of fluctuations described by Eq. (1) carries the remarkable implication that the effective interfacial width w measured in a thin film of coexisting phases will also depend on D. This is because we expect the lateral correlation length $\xi_\parallel$ to provide a cutoff for the spectrum of capillary wave excitations of the interface normal to the film thickness. As is well known [11,12], a free interface between coexisting phases has a width w broadened by these capillary wave excitations [we define w by $w = (\phi_2 - \phi_1)/(d\phi/dz)_{\max}$, $\phi(z)$ being the *A* volume fraction profile normal to the interface]. If gravity can be neglected, on a lateral length scale L this broadening would be described by [11–13]

$$(w/2)^2 = \xi_b^2[1 + \ln(L/\xi_b)], \qquad (2)$$

where we have assumed that the intrinsic width is ξ_b, which also acts as a cutoff for short wavelength capillary waves in Eq. (2). Now the gap caused by Eq. (1) for large wavelengths simply means that L in Eq. (2) needs to be replaced by $\xi_\parallel$, provided $\xi_\parallel$ is less than the lateral size $L_{\max}$ of the sample, i.e.,

$$(w/2)^2 = \xi_b^2 + \xi_b D/4 \qquad (3)$$

invoking $\kappa^{-1} = \xi_b$. Equation (3) implies $w \propto \sqrt{D}$ for large D (if $L_{\max} \to \infty$).

Apart from prefactors of order unity [13], which are possibly lost in this rough argument, this relationship is completely general and should hold for all types of thin films of fluid or solid mixtures on suitably selective substrates, and other systems in the Ising "universality class" [7,12]. In addition, generalizations to surface effects on more complicated orderings (e.g., orientational order in liquid crystals, etc.) can be envisaged. Despite this generality, and despite the widespread practical importance of interfacial phenomena, any experimental evidence for

the prediction that the interfacial width increases with film thickness has, to date, been completely lacking. In this Letter we present data based on nuclear reaction analysis (NRA) depth profiling of thin films of polymer mixtures which confirm this prediction. We substantiate this claim by simulation results for the nearest neighbor Ising model, which have a striking qualitative similarity to the experiments.

The components of the binary (*AB*) mixture used were two random copolymers, of mean microstructure $[(C_4H_8)_{1-x}(C_2H_3(C_2H_5))_x]_N$, N being the degree of polymerization, with $x = 0.75$ (*A*), $N_A = 1625$, and $x = 0.66$ (*B*), $N_B = 2030$. Polymer *A* is partly deuterium labeled (40% deuterium atoms) for the NRA profiling. The thermodynamic behavior of this pair has been well characterized [14]: its bulk critical temperature and bulk critical volume fraction (of *A*) are $T_{cb} = 374$ K and $\phi_{cb} = 0.61$, respectively. Such a polymer mixture provides an attractive model system, because for N of the order 10^3 the length scale is sufficiently large already in the bulk (ξ_b is of the order of 10 nm), which facilitates NRA profiling. At the same time T_w falls far below [14–16] T_{cb}, enabling a convenient choice for the temperature $T_0 < T_{cb}$ at which the interface between coexisting phases is established, $T_0 = 356$ K (far above the glass transitions T_g of the two components [17], $T_g^A = 227$ K, $T_g^B = 219$ K). Coexisting phases were prepared by spin-casting films of a mixture of the components at a composition $\phi = 0.60 \pm 0.01$, close to ϕ_{cb}, and annealing the films to equilibrium at T_0. At this annealing temperature the mixtures undergo phase demixing, and at equilibrium the *A*-rich phase is preferentially attracted to the polymer-air surface [14,15]. The phase interface is then parallel to the surfaces, and is roughly in the middle of the films. Overall film thickness was in the range $D = 80–1200$ nm.

Figure 1 shows typical composition profiles of two films in this range, as determined by NRA. The measured data are a convolution of the actual profile with the depth-dependent spatial resolution $\delta(D)$. Thus a precise knowledge of $\delta(D)$, which increases with D and is of the same order as w, is essential for evaluating the interfacial width. $\delta(D)$ was determined in a comprehensive separate study in which single-component deuterated polymer films of thickness D, cast on smooth gold-covered silicon wafers, were profiled in the range $50 < D < 1500$ nm for a large number of different D values. The measured width of the (sharp) polymer-solid interface was highly reproducible at each D value and yielded $\delta(D)$ to within $\pm 1–2$ nm over most of the range [18]. w (and its uncertainty limits) was determined from a least squares fit to the data, as detailed in Fig. 1.

The main qualitative feature emerges at once: The interfacial width $w = 27$ nm in the thicker film [$D = 430$ nm, Fig. 1(a)] is significantly larger than its value $w = 14$ nm in the thinner film [$D = 160$ nm, Fig. 1(b)]. Figure 2
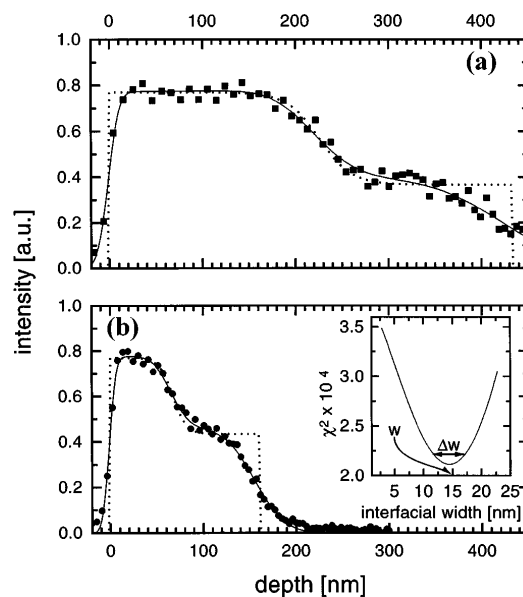

FIG. 1. Typical composition-depth profiles of films of an *A*-rich phase at the air interface (depth = 0) coexisting at $T_0 = 356$ K with an *A*-poor phase on top of a silicon wafer [at depths $D = 430$ and 160 nm, respectively for (a) and (b)], obtained using NRA [22–24] based on the reaction ^{3}He + ^{2}H $\rightarrow$ ^{4}He + ^{1}H + 18.35 MeV. Backward angle detection of ^{1}H enabled an optimal spatial resolution of some 4 nm at the air surface [22], decreasing due to straggling at greater depth. The dotted curves are the theoretical profiles $\phi(z) = \frac{1}{2}\{\phi_1 + \phi_2 + (\phi_2 - \phi_1)\tanh[(z - z_0)/w]\}$, where z_0 is the midpoint of the interfaces between the coexisting phases. The solid lines are the best fit to the data obtained by convoluting the theoretical profiles with the independently determined depth-dependent resolution $\delta(D)$. The inset shows how the squared residuals χ^2_{res} vary with w used for the fit: The best-fit value of w corresponds to the minimum $(\chi^2_{res})_{min}$; the quoted estimated error corresponds to the limits $\Delta\chi^2_{res}/(\chi^2_{res})_{min} = 0.05$. Both are indicated on the inset. As a consistency check w was also determined in a number of cases by quadrature subtraction: $w = [w_m(D)^2 - \delta(D_i)^2]^{1/2}$, where $w_m(D)$ is the width of the interface at depth D_i in a film of thickness D, obtained by fitting to the as-measured profile, and $\delta(D_i)$ is the corresponding resolution at that depth. The values of w determined by these two approaches were fully consistent. (a) Film thickness $D = 430$ nm, $w = 27 \pm 7$ nm. (b) Film thickness $D = 160$ nm, $w = 14.4 \pm 3$ nm.

summarizes the data over the entire D range studied: Within the scatter, there is a clear and striking monotonic increase of w with D, as envisaged in Eq. (3).

Also included in Fig. 2 is the prediction of Eq. (3). For this purpose, we use the standard mean field estimate for the correlation length in polymer blends [19],

$$\xi_b = \frac{a}{6} \Bigg/ \sqrt{\frac{1 - \phi}{2_{N_A}} + \frac{\phi}{2_{N_B}} - \chi\phi(1 - \phi)} \qquad (4)$$

where the length a is an effective statistical segment length in the blend and χ is the segment-segment interaction parameter. ξ_b is estimated [20] to be in the range
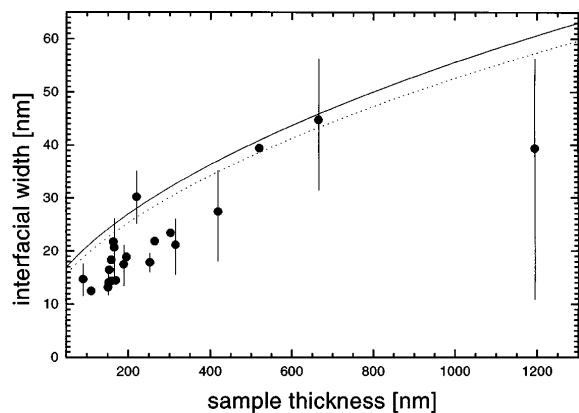
FIG. 2. Plot of w vs D for a blend of the olefinic copolymers A, B as described in the text, at $T_0 = 356$ K, extracted from profiles such as shown in Figs. 1(a) and 1(b). The curves correspond to Eq. (3) as described in the text, using $\xi_b = 10.6$ nm (broken curve) and $\xi_b = 11.8$ nm (full curve).

10.6–11.8 nm. As expected, this is of the same order as the gyration radii of the components [14] ($R_{gA} \approx 9.3$ nm, $R_{gB} \approx 11.6$ nm). We note that Eq. (3) describes the data well qualitatively, and correctly predicts the order of magnitude of the effect. For D comparable to ξ_b we would expect $w \propto D$, as discussed also below; in addition, for $D \to 0$ the interfacial width must also vanish, while Eq. (3) predicts a finite value ($2\xi_b$) at $D = 0$. Hence the data for $D \lesssim 160$ nm fall distinctly below Eq. (3). We also remark that constraints that arise due to the film thickness becoming comparable with the chain coil size have not been taken into account in the model: These are important at the lowest D values examined, and may be responsible for some of the discrepancy.

Figure 3 presents a test of the above ideas [Eq. (3)] for the Ising model, reanalyzing data used in Refs. [6,10]. We note that the data are at a value $T/T_{cb} = 0.9554$, close to the value $T_0/T_{cb} = 0.95$ for the experimental couple shown in Figs. 1 and 2. Figure 3(a) shows that the profile gets broader with increasing D, and is compatible [inset to Fig. 3(a)] with the result that $w \propto \sqrt{D}$. Indeed, the increase of w with D, shown in Fig. 3(b), appears qualitatively rather similar to that seen in Fig. 2. While there is not a full quantitative agreement with Eq. (3), the order of magnitude of the effect is again (as in the experiments) predicted correctly. The source of the discrepancy may be the mean field identification $\kappa^{-1} = \xi_b$, which is known to fail in the Ising model [6,9,10]. Recently it has been suggested [9] that one should instead use $\kappa^{-1} = \xi_b(1 + \omega/2)$, where ω is the capillary parameter [13] of the Ising model [26] ($\omega = k_B T/4\pi \xi_b^2 \Sigma$, Σ being the interfacial tension [21], $\omega \approx 0.86$). Figure 3(b) shows that this choice improves the agreement somewhat. Of course, Eq. (3) is not expected to be accurate for values of D comparable to $2\xi_b$, when the profile is significantly distorted; see Fig. 3(a) (and, as noted
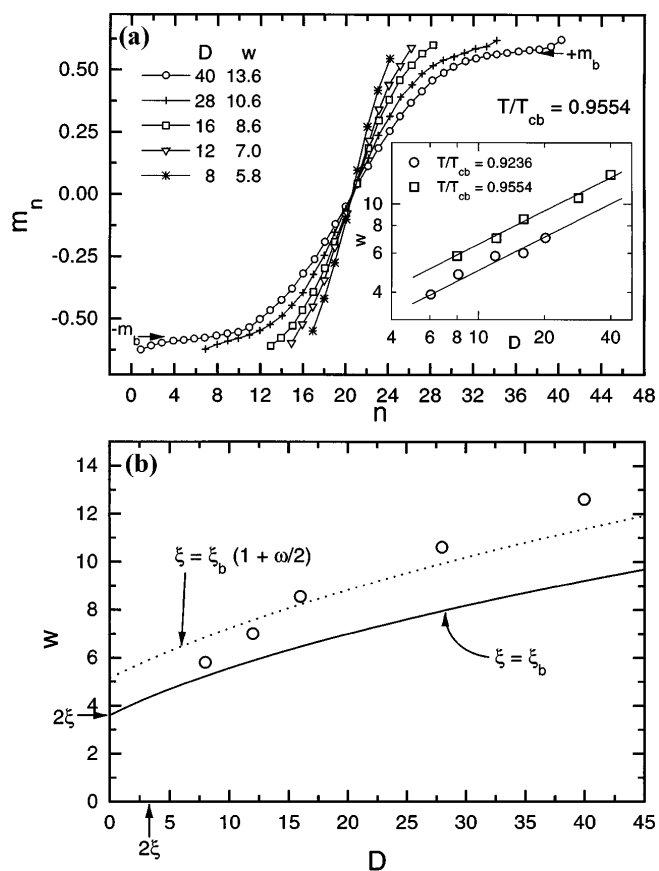

FIG. 3. (a) Profile of the layer magnetization m_n vs layer index n of simple cubic Ising films with five different thicknesses D (in units of the lattice spacing), adapted from Refs. [6,10], at $J/k_B T = 0.232$ (J being the exchange constant, note $J/k_B T_{CB} \approx 4.511$) [25]. At the free surface $n = 1$ a field $H_1 = -0.55J$ is applied, while at the other surface at $n = D$ acts an opposite field $H_D = +0.55J$. Values of the corresponding bulk order parameters $\pm m_b$ (known from independent work [25]) are shown by arrows. Widths w are extracted from the slopes of the profiles in their center and are quoted in the table. Inset: log-log plot of w vs D for two choices of temperature as indicated; the lines show $w \propto D^{1/2}$. (b) Plot of w vs D for $T/T_{cb} = 0.9554$ in the 3D Ising model, as observed from the simulation (circles) and compared to Eq. (3), full curve, using [26] $\xi_b = 1.80$ lattice spacings. The broken curve uses a formula accounting phenomenologically for fluctuation corrections, $w^2 = \kappa^{-2} + \kappa^{-1}D/4$, with $\kappa^{-1} = \xi_b(1 + \omega/2)$, $\omega \approx 0.86$ being the capillarity parameter [21] in the Ising model.

above, we expect $w \to 0$ as $D \to 0$). In addition, our Monte Carlo data for the largest choice of D may be systematically in error, since L_{max} ($= 128$ in this case) was probably too small.

A number of remarks are in order. One caveat to be made about Eqs. (1)–(3) with relation to the results of the present experiments (Fig. 2) is that they apply only for short range forces between the wall and the polymer blend. For long range forces (e.g., van der Waals forces) one expects a power law rather than the exponential variation

with D in Eq. (1), and then the increase of the width w with D only would be logarithmic. There is one additional feature worth noting: For $D \approx 600$ nm (taking $\xi_b = 11$ nm) the length $\xi_\parallel \approx 1$ cm; i.e., it becomes comparable with the lateral linear dimension L_{max} of our sample, and hence one should see a leveling off in the w vs D curve at higher sample thickness ($D > 600$ nm). While the data in this regime have a higher intrinsic uncertainty due to the higher straggling, there does appear to be some suggestion in the data of such a leveling off. One might also ask whether a fluctuation correction $(1 + \omega/2)$ is needed, as in the Ising model: We have neglected this, since ω is believed to be of order $1/\sqrt{N}$ for polymers [16]. Finally, fluctuations of the polymer-air interface have also not been considered; they are controlled by the much smaller length a rather than ξ_b in Eq. (2).

To summarize, we have demonstrated directly, both by composition depth profiling of a liquid-liquid interface and by Ising model simulations of thin layers with competing walls, that the interfacial width between coexisting phases increases quasilinearly with film thickness. This result is consistent with the recent prediction that the correlation length for compositional fluctuations parallel to an interface diverges exponentially with the dimensions of the coexisting adjacent layers. It confirms experimentally a new type of finite-size effect for the structure of interfaces in layered phases.

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